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THERMAL CHEMISTRY

Thermochemische Untersuchungen. Von Julius Thomsen, Dr. Phil. et Med., &c. Volumes I., II., and III. (Leipzig : Johann Ambrosius Barth, 1882-83.)

A PAPER was published in this journal a short time ago calling attention to "The Backward State of Chemistry in England" (vol. xxviii. p. 613) ; the writer regrets that so little attention is paid to the chemistry of the carbon compounds, and that so much time is spent in our chemical schools in elementary and routine instruction. In the second of these regrets I can thoroughly sympathise ; our so-called students of chemistry are becoming mere machines which perform, and generally perform badly, mechanical processes known as qualitative and quantitative analyses. We hear complaints from physical laboratories that practical physics is taught in an unsystematic manner ; we sometimes have comparisons drawn between the desultory methods of teaching pursued in these laboratories and the orderly and systematic courses of practical chemistry conducted in the workrooms of the sister science. But I am afraid it is rather the chemist who is to be pitied: his method is too methodical; it seems to succeed because it neglects the really scientific aspects of chemistry. Chemistry is a great branch of science ; but what is the so-called practical chemistry of the schools or the examination ? It is but a weary round of dull repetition ; it consists of obtaining black precipitates, and yellow precipitates, and colourless precipitates, precipitates which are soluble and those which are insoluble ; it occupies itself with filtering and washing, and drying, and burning, and weighing ; it has little or no connection with the problems which belong to the science of chemistry. But when the author of the article to which reference has been made attributes the backward state of chemistry in England to the comparatively small amount of attention which is given to organic chemistry, I find myself unable to agree with him. I think we are apt to be dazzled by such things as the synthesis of indigo, or the artificial manufacture of alizarin : we forget to inquire whether the study of organic chemistry has in recent years added any great general principle to chemical science. The conception of the valency of elementary atoms is certainly an outcome of the study of the carbon compounds, or rather of the application of the atomic theory to this study ; but have we not of late made too much of this conception ? has it not rather stopped than aided inquiry ? is it not time we had given up our "bonds," our "units of affinity," which are chiefly remarkable as being changeable almost at pleasure ? Organic chemistry, as pursued in the German laboratories, it seems to me, has almost if not quite entered on the same path as that which has led qualitative and quantitative analysis to so sad a fall : it is in danger of ceasing to be a branch of science and of becoming an art of manufacture. Any student who goes through the course of preparation of organic compounds, systematised so well in the laboratories of the German universities and elsewhere, is ready to manufacture new compounds by the score ; the difficulty consists in not making such compounds. There are whispers abroad that he who is not in the trade is regarded by the German professors as "no chemist."

I think the evil lies deeper : we are so anxious to act that we have no time to think. The chemist may gain a kind of reputation by making new compounds ; the process requires no thought, no scientific training, no originality. It has also something to be said in its favour. Nature is so vast that we can scarcely hope to gain any accurate knowledge save by attacking the problems in detail. In chemistry, as in other branches of science, we must be content to gain "a series of small victories" over nature. But in fighting nature in detail we are apt to lose sight of general principles by the help of which alone can empiricism become science. I think that in chemistry, and more especially perhaps in organic chemistry, we are specialising too much : we are trying to solve large and complex problems by a series of small attacks all delivered from the same point. What then is the remedy ? I would answer : Vary the points of attack ; remember that the victory is to be gained only by boldness, and that it is emphatically worth gaining. Do not let chemistry remain the battlefield of the Philistines, but enliven it with the true spirit of science, with that spirit which will not believe that the universe is a "rubbish-heap of confused particulars," but will rather regard it as a vast organism in which while "everything is distinct yet [is] nothing defined into absolute independent singleness."

That the points from which the problems of chemistry may be attacked are many is witnessed by the book before us. Why is there no handbook of thermal chemistry in English ? Will not some one at least translate Naumann's "Handbuch"? M. Thomsen has for years been known as one of the two great workers in the field of thermal chemistry ; his contributions to this branch of science have been numerous and important ; we cannot be too thankful that he has gathered these contributions together, and arranged and digested them in this series of volumes, which must remain as the groundwork of the science. Three volumes have appeared, and a fourth (to treat of organic compounds) is promised. Let me try to give some account of one or two points in Thomsen's work.

The notation of thermal chemistry is simple : Let r = the thermal value (stated in gram-units) of a chemical change ; if the change consist in the formation of a definite quantity of a compound $X_a Y_b Z_c$—made up of *a* parts of X, *b* parts of Y, and *c* parts of Z—then

$$r = [X^a, Y^b, Z^c] + ;$$ [1]

if the same compound is produced in presence of a large quantity of water, then

$$r = [X^a, Y^b, Z^c, Aq] + ;$$

if the same substance already formed is dissolved in an unlimited quantity of water, then

$$r = [X^a Y^b Z^c, Aq] +.$$

The general expressions for the production and decomposition of a compound $X_a Y_b$ are

$$(1)\ X_a + Y_b = X_a Y_b + (X^a, Y^b) ;$$

and

$$(2)\ X_a Y_b = X_a + Y_b - (X^a, Y^b).$$

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[1] Thomsen always writes the indices above the elementary symbols when these symbols occur in thermal equations

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If the compounds X Y and Z V react to produce X Z and Y V then

$$r = [X, Z] + [Y, V] - [X, Y] - [Z, V].$$

These equations illustrate the methods by which the thermal value of a chemical change can be indirectly calculated. The total loss of energy by a chemical system in passing from a definite initial to a definite final state is independent of the intermediate states; assuming, as we may do for most purposes, that the total loss of energy is measured by the quantity of heat evolved, it follows that the total thermal change accompanying a chemical change depends only on the initial and final states of the system. Hence, if we have series of reactions beginning with the same materials in the same condition, and ending with the same products in the same condition, and if all the thermal changes in one series may be measured, and all except one in the other series may be measured, it follows that we can calculate the thermal value of the unknown member of the second series of changes. Thus, it is required to determine the thermal value of the synthesis of 46 grams of formic acid (CH_2O_2). Twelve grams of carbon, 2 of hydrogen, and 48 of oxygen combine to produce 44 grams of carbon dioxide and 18 grams of water: but the same quantities of the same materials might theoretically be combined to produce 46 grams of formic acid, and then from this, 44 grams of carbon dioxide + 18 grams of water would be produced. The following are the thermal values of the various parts of these two series of changes :—

$$[C, O^2] = 96{,}960 \text{ gram-units} + ; [H^2, O] = 68{,}360 + ;$$
$$[CH^2O^2, O] = 65{,}900 + ;$$

but

$$[C, O^2] + [H^2, O] = [C, H^2, O^2] + [CH^2O^2, O] = 165{,}320 +$$
$$\therefore [C, H^2, O^2] = [C, O^2] + [H^2, O] - [CH^2O^2, O] = 99{,}420 + .$$

Such calculations sometimes become very complex; corrections must frequently be introduced for quantities of heat evolved or absorbed during purely physical changes which form integral parts of the cycle of chemical change under investigation.

The thermal study and comparison of classes of chemical changes leads to the conclusion that a chemical change which is accompanied by considerable loss of energy to the changing system will generally occur, unless prevented by the action of forces external to the system. This generalisation, vague though it be, helps to explain many classes of chemical reactions, *e.g.* the action of concentrated and dilute solutions of hydriodic acid on sulphur, and on many hydroxyl-containing carbon compounds; and the action of sulphuretted hydrogen in precipitating certain metallic sulphides in the presence of acid, and others only form alkaline liquids.

Thomsen has devoted much time and care to the thermal investigation of the mutual actions of acids and bases: the greater part of his first volume is devoted to this inquiry. The "heat of neutralisation of an acid by a base" is defined as the number of gram-units of heat evolved on mixing equivalent quantities in grams of the acid and base in dilute aqueous solution, the products of the action being also soluble in water. Thomsen employs a solution of 2 NaOH (grams) in about 200 H_2O (grams) as the standard base: he measures the thermal values of the following reactions :—

[2NaOH Aq, 2HX Aq] in the case of a monobasic acid.
[2NaOH Aq, H_2X Aq] „ „ dibasic „
[2NaOH Aq, $\frac{2}{3}H_3X$ Aq] „ „ tribasic „
[2NaOH Aq, $\frac{1}{2}H_4X$ Aq] „ „ tetrabasic „

The commoner acids may be broadly divided into four groups, according to the values of the "heats of neutralisation." This value is for Group I. about 20,000 gram-units; II., about 25,000; III., about 27,000; and IV., about 30,000 gram-units. The study of heats of neutralisation has led Thomsen to the conception of the *avidity* of an acid, *i.e.* the striving of one acid to displace another from its combination with a base. Thus, when equivalent quantities of NaOH, $HNO3$, and H_2SO_4 are mixed in dilute aqueous solutions, two-thirds of the NaOH combines with the HNO_3, and one third with the H_2SO_4; the *avidity* of HNO_3 for NaOH is said to be twice as great as that of H_2SO_4 for the same base. HNO_3 in aqueous solution is therefore a *stronger acid* than H_2SO_4.

Measurements of the heats of neutralisation of monobasic, dibasic, *n*-basic acids has led Thomsen to classify some of these acids in ways different from those generally adopted in the text-books. His results as regards dibasic and tribasic acids may be thus summarised :—

Dibasic Acids

Group I. Typical formula $R\,H_2$ *e.g.* $SiF_6 . H_2$
„ II. „ „ $R(OH)_2$ *e.g.* $SO_2(OH)_2$
„ III. „ „ $R(OH)H$. *e.g.* $SO_2(OH)H$.

Tribasic Acids

Group II. Typical formula $R(OH_3)_3$. *e.g.* $C_4H_5O_4(OH)_3$.
„ III. „ „ $HR(OH)H$. *e.g.* $HPO_3(OH)H$.

These examples will serve to show the suggestiveness of the results of thermal chemistry. Thomsen's three volumes teem with suggestions: his results throw light on such questions as are connoted by the expressions allotropy, molecular compounds, classification of elements and compounds, isomerism, and affinity.

It is in examining the subject of chemical affinity from the point of view of thermal chemistry that one becomes aware of the complexity of the problems included under this expression.

From the following numbers,

$$[H, Cl] = 22{,}000 + ; [H, Br] = 8440 + ; [H, I] = 6050 - ;$$

it might be concluded that the affinity of chlorine for hydrogen is much greater than that of bromine, and that the affinity of iodine for hydrogen is much less than that of bromine. But these thermal equations are not comparable; at ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid; hence, on this ground alone, no precise conclusions can be drawn from the above data regarding the relative affinities for hydrogen of the three halogen elements. Again, looking at the numbers,

$$[C, O] = 28{,}600 + ; \; [C, O^2] = 97{,}000 + ,$$

it might be said that when oxygen combines with carbon in quantities of 16 grams at a time, the union of the second parcel of 16 grams is attended with evolution of much more heat than accompanies the addition of the first parcel of 16 grams. But measurement of the heat of oxidation of carbon monoxide, $[CO, O] = 68{,}400 +$, at once negatives this conclusion, and rather points to the number 68,400 × 2 136,800 as representing the thermal value of the transaction, $C + O_2 = CO_2$, where C represents 12 grams of gaseous carbon.

In the ordinary chemical notation almost every chemical change is represented as much simpler than it really is; no indication is given of the fact that in most cases an *excess* of one or other of the reacting substances must be used. Thus the reaction usually written

$$AgCl + HI \text{ (gas)} = AgI + HCl$$

would more correctly represent the distribution of the reacting bodies were it written

$$xAgCl + x'HI = xAgI + x'HCl + (x - 1)AgCl + (x - 1)HI.$$

If it is assumed that in the thermal study of a chemical reaction allowance is made for all the purely physical changes which accompany the chemical change, for the influence of the masses of the reacting substances and for the possible formation and decomposition of molecular groups during the reaction, there yet remains the consideration that heat is lost or gained to the system in the decompositions and formations of elementary molecules, which decompositions and recompositions may form parts of the entire change under examination. Thus, take the comparatively simple reaction

$$2H_2O + Cl_4 = 4HCl + O_2;$$

expanded thermally we have

$$r = 4[H, Cl] + [O, O] - 2[H^2, O] + 2[Cl, Cl].$$

Even the apparently most simple case, the union of two elements, is more complex than at first sight appears. $[H^2, Cl^2] = 44{,}000 +$ simply tells that 2 grams of hydrogen combine with 71 grams of chlorine, and that 44,000 gram-units of heat are evolved. But if we wish to apply these data to questions concerning the affinity of chlorine for hydrogen, we must remember that affinity is the name given to the stress between atoms when regarded from the point of view of one kind of the reacting atoms. Hence, remembering that the molecules of hydrogen and chlorine are diatomic, we must amplify the equation $[H^2, Cl^2] = 44{,}000 +$, and write it thus—

$$r = 2[H, Cl] - [H, H] - [Cl, Cl] = 44{,}000 +;$$

but the value to be assigned to two of the terms in this equation are unknown. Until we are able to assign approximate values to the thermal changes accompanying the decompositions of elementary molecules and the combinations of elementary atoms, we shall not be in a position to apply thermal data to the subject of affinity, provided, that is, we use this term in its most precise meaning.

The statement of Berthelot in the "Essai de Mécanique Chimique," that the quantity of heat evolved in a reaction measures the sum of the physical and chemical changes which occur in that reaction, and furnishes a measure of the chemical affinities, is evidently untrue if we assign any precise meaning to the term "affinity." But if we use this term in a wide sense as summing up the various actions and reactions (other than those which are purely physical) which together constitute any given chemical change, then we may perhaps say that thermal measurements of comparable reactions are also relative measurements of the affinities of the reacting substances. It is in some such sense as this that the term "affinity" is used by Thomsen in his thermal researches on the relative affinities of the non-metallic elements (vol. ii.).

It is worthy of remark that Thomsen's arrangement of the commoner acids in order of relative affinities agrees very well with that given by Ostwald as the result of his investigations conducted on altogether different lines and by very different methods.

If thermal measurements of chemical changes really represent the sums of various partial changes, some of which have a positive and others a negative value, then it becomes doubtful whether any practical result is to be looked for from the application of Berthelot's *law of maximum work*, which runs thus:—

"Every chemical change, accomplished without the addition of energy from without the system, tends to the formation of that body or system of bodies the production of which is accompanied by evolution of the maximum quantity of heat."

Thomsen puts this "law" in a somewhat different form: he says, "Every simple or complex reaction of a purely chemical kind is accompanied by evolution of heat." Thomsen explains that by a purely chemical process he means one which is accomplished without addition of energy from sources external to the system, and consists in the "striving of atoms towards more stable equilibrium." But there are, I think, two principal objections to this statement. Actions "of a purely chemical kind," as thus defined, do not actually occur except as parts of cycles of reactions wherein are included changes not of a "purely chemical kind." And, secondly, we have at present no means of measuring the thermal values of those purely chemical actions—*i.e.* on Thomsen's view, atomic actions—but are obliged to include their values in the total value assigned to the complete cycle of operations which we term a chemical reaction.

Thomsen has it is true attempted to assign thermal values to the decomposition of the molecule of carbon into atoms and the recombination of atoms of carbon to form molecules. The pages of NATURE are scarcely suitable for a detailed discussion of Thomsen's methods; it seems to me, and I think to some others who have tried to follow Thomsen's arguments, both in the second volume of his "Untersuchungen" and also in the original papers in the *Berichte* and elsewhere, that these arguments really bristle with assumptions, and that a comparison of the results deduced by Thomsen with the actual calorimetric measurements obtained by himself and others is sufficient to throw grave doubt on the validity of those assumptions on which his arguments are based. One general result which appears to me to follow from Thomsen's investigation is that the time has come when we may with great advantage give up such expressions as "the carbon atom has four bonds," "such or such atoms are held by double links," and indeed the whole of that unscientific pseudo-dynamical nomenclature which has grown up around the vague and indefinable conception of *atomic bonds.*

There are many other points of interest in Thomsen's "Untersuchungen"; but I have said enough I trust to show the importance and the remarkable suggestiveness of these volumes; and also to establish the statement that the great advances of the future in chemistry are to be looked for, not so much in the domain of organic chemistry as in the application of the methods and generalisations of the science of matter and motion to the problems which we call chemical.

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